BALLISTIC-RESISTANT MOULDED ARTICLE AND A PROCESS FOR THE MANUFACTURE OF THE MOULDED ARTICLE

The invention relates to a ballistic-resistant moulded article containing a compressed stack of monolayers, with each monolayer containing unidirectionally oriented reinforcing fibres and at most 30 wt.% of a plastic matrix material and with the fibre direction in each monolayer being rotated with respect to the fibre direction in an adjacent monolayer. The invention also relates to a process for the manufacture of the moulded article. The ballistic-resistant moulded article may be used in, for instance, helmets, as inserts in bullet-proof vests, as armouring on military vehicles and in ballistic-resistant panels.

A ballistic-resistant moulded article of this type is disclosed in WO 89/06190. The known ballistic-resistant moulded article affords fairly good protection against impacts of projectiles such as shrapnel or bullets. The level of protection is quantified by means of the Specific Energy Absorption (SEA), a measure of the amount of energy that can be absorbed by a moulded article on impact of a projectile per unit areal density of the moulded article. Fairly good protection by the known moulded article on impact of a bullet is intended to mean an SEA value of from about 30 Jm^2/kg to maximum 65 Jm^2/kg. The March 1992 "Ballistics" leaflet of Messrs Allied-Signal Inc., Petersburg, Virginia, quotes as highest SEA level an SEA of 65 Jm^2/kg on impact of a 7.62 x 39 Mild Steel Core P.S. Ball M1943. This SEA level has been achieved after years of optimization and was regarded by ballistics experts as being very high.

Nevertheless, there continues to be a great need for ballistic-resistant moulded articles that can offer increased protection against impacts of projectiles of various kinds, especially against

5 projectiles in the form of bullets.

The inventors of the present invention have found that this object is achieved by the density ρ_P of the compressed stack in the ballistic-resistant moulded article being at least 98.0% of the theoretical maximum

10 density.

The theoretical maximum density ρ_{th} is calculated using the following formula:

$$\rho_{th} = \rho_f \, m_f + \rho_k \, m_k$$

where

15 ρ_f = density of the fibres

ρ_k = density of the plastic

m_f = mass fraction of the fibres in the compressed stack

m_k = mass fraction of the plastic in the

20 compressed stack

Surprisingly, a ballistic-resistant moulded article of the invention has an SEA value of at least 75 Jm^2/kg on impact of a 7.62 x 39 Mild Steel Core P.S.

25 Ball M1943.

The percentage of the theoretical maximum density is hereafter referred to as the relative density. Preferably, the relative density of the compressed stack is at least 98.5%, more preferably at

30 least 99.0% and most preferably at least 99.5%. In this way, a ballistic-resistant moulded article having an even better SEA value is obtained. More preferably, the SEA value is at least 90, even more preferably at least 110 Jm^2/kg, most preferably at least 120 Jm^2/kg.

35 The density of the ballistic-resistant moulded article can be determined in a manner known to one skilled in the art. A suitable, accurate method is

described in ASTM D 792-91. Another suitable method for flat or slightly flexed moulded articles comprises measurement of the density by measuring the weight and accurately measuring the volume with the aid of a
5 Vernier calliper. By this measurement, if accurately performed, the density can be determined with a standard deviation of 0.2-0.4%.

The SEA is defined by $0.5 . m . v_{50}^2 / AD$, where m is the mass of the projectile. The v_{50} is the velocity
10 of the projectiles fired at the moulded article at which 50% of the projectiles fully penetrate the moulded article, AD is the areal density of the moulded article.

Owing to the surprisingly high SEA achieved,
15 not only moulded articles with an unheard-of level of protection for a given weight of the moulded article are now available but also moulded articles affording the same level of protection as the known moulded article at a significantly lower weight. Low weight per
20 unit area is of great importance in many applications. This is the case, for instance, in the field of personal protective equipment such as helmets, shields, shoes and the like. Low weight is also essential for the application of ballistic-resistant moulded articles
25 in for instance helicopters, motorcars and high-speed, highly manoeuvrable combat vehicles.

The areal density of the moulded article depends on the desired level of protection. Preferably, the areal density is between 10 and 40 kg/m^2. Below 10
30 kg/m^2, the level of protection is inadequate for most threats, above 40 kg/m^2 the weight will often be too high, especially for body protection.

In the context of the present application "monolayer" means a layer of substantially parallel
35 reinforcing fibres embedded in a plastic matrix material. The term "matrix material" means a material which binds the fibres together and which wholly or

partially encapsulates the fibres. Such monolayers (usually called prepregs by one skilled in the art) and methods of obtaining such a monolayer are disclosed in for instance EP-B-0.191.306 and WO 95/00318. A

5   monolayer may be obtained by for instance pulling a number of fibres from a fibre bobbin frame over a comb so that they are oriented in coplanar and parallel fashion in one plane and then impregnating the fibres with the plastic. In this process, fibres may be used

10   that have previously been coated with a polymer other than the plastic matrix material in order to, for instance, protect the fibres during handling or in order to obtain better adhesion of the fibres onto the plastic of the monolayer. Preferably, uncoated fibres

15   are used. Impregnation of the reinforcing fibres with the plastic matrix material can be effected by applying one or more films of the plastic to the top, bottom or both sides of the plane of the fibres and then passing these, together with the fibres, through a heated

20   pressure roll. Preferably, however, the fibres, after being oriented in coplanar, parallel fashion in one plane, are coated with an amount of a liquid substance containing the plastic matrix material of the monolayer. The advantage of this is that more rapid and

25   better impregnation of the fibres is achieved. The liquid substance may be for example a solution, a dispersion or a melt of the plastic. If a solution or a dispersion of the plastic is used in the manufacture of the monolayer, the process also comprises evaporating

30   the solvent or dispersant.

"Reinforcing fibre" here means an elongate body whose length dimension is greater than the transverse dimensions of width and thickness. The term "reinforcing fibre" includes a monofilament, a

35   multifilament yarn, a tape, a strip, a thread, a staple fibre yarn and other elongate objects having a regular or irregular cross-section. Any natural or synthetic

fibre may in principle be used as reinforcing fibre.
Use may be made of for instance metal fibres, semi-
metal fibres, inorganic fibres, organic fibres or
mixtures thereof. For application of the fibres in
5   ballistic-resistant moulded parts it is essential that
the fibres be ballistically effective, which, more
specifically, requires that they have a high tensile
strength, a high tensile modulus and/or high energy
absorption. It is preferred for the fibres to have a
10   tensile strength of at least 1.2 GPa and a tensile
modulus of at least 40 GPa.

Suitable inorganic fibres having a high
tensile strength are for example glass fibres, carbon
fibres and ceramic fibres. Suitable organic fibres
15   having a high tensile strength are for example aramid
fibres, liquid crystalline polymer fibres and fibres of
for instance polyolefins, polyvinylalcohol,
polyacrylonitrile which are highly oriented such as
those obtained by means of a gel spinning process.

20   An extensive enumeration and description of
fibres that may be used in the monolayer are given in
WO 91/12136 (line 23 on page 6 to line 8 on page 12).

Homopolymers and copolymers of polyethylene
and polypropylene are particularly suitable as
25   polyolefins. Furthermore, the polyolefins used may
contain small amounts of one or more other polymers, in
particular other alkene-1-polymers.

It is preferred for the reinforcing fibres in
the monolayer to be high-drawn fibres of high-molecular
30   weight linear polyethylene. High molecular weight here
means a molecular weight of at least 400,000 g/mol.

Linear polyethylene here means polyethylene
having fewer than 1 side chain per 100 C atoms,
preferably fewer than 1 side chain per 300 C atoms. The
35   polyethylene may also contain up to 5 mol % of one or
more other alkenes which are copolymerisable therewith,
such as propylene, butene, pentene, 4-methylpentene,

octene.

Preferably, use is made of polyethylene
fibres consisting of polyethylene filaments prepared by
a gel spinning process as described in for example GB-
5   A-2042414 and GB-A-2051667. This process essentially
comprises the preparation of a solution of a polyolefin
of high intrinsic viscosity, spinning the solution to
filaments at a temperature above the dissolving
temperature, cooling down the filaments below the
10   gelling temperature so that gelling occurs and drawing
the filaments before, during or after removal of the
solvent.

The shape of the cross-section of the
filaments can be selected here through selection of the
15   shape of the spinning aperture.

Preferably, the monolayer contains
reinforcing fibres, preferably the aforementioned
strong polyethylene fibres, with a denier per filament
(dpf) greater than or equal to 1.5. Most preferably,
20   use is made of multifilament yarns of ultrahigh
molecular weight linear polyethylene with an intrinsic
viscosity of at least 5 dl/g, determined in decalin at
135°C, and a yarn titre of at least 50 denier, with the
yarn having a tensile strength of at least 35 cN/dtex
25   and a tensile modulus of at least 1000 cN/dtex and the
filaments having a cross-section aspect ratio of at
most 3. The use of these fibres has been found to
improve the high level of protection of the ballistic-
resistant panel of the invention still further.
30   The plastic matrix material may wholly or
partially consist of a polymer material, which
optionally may contain fillers usually employed for
polymers. The polymer may be a thermoset or
thermoplastic or mixtures of both. Preferably a soft
35   plastic is used, in particular it is preferred for the
plastic matrix material to be an elastomer with a
tensile modulus (at 25°C) of at most 41 MPa.

Preferably, the elongation to break of the plastic is greater than the elongation to break of the reinforcing fibres. The elongation to break of the matrix preferably is from 3 to 500%.

5   Thermosets and thermoplastics that are suitable for the monolayer are listed in for instance WO-A-91/12136 (line 26, page 15 to line 23, page 21). Preferably, vinylesters, unsaturated polyesters, epoxides or phenol resins are chosen as matrix material

10   from the group of thermosetting polymers. These thermosets usually are in the monolayer in partially set condition (the so-called B stage) before the stack of monolayers is cured during compression of the ballistic-resistant moulded article. From the group of

15   thermoplastic polymers polyurethanes, polyvinyls, polyacryls, polyolefins or thermoplastic, elastomeric block copolymers such as polyisoprene-polyethylene-butylene-polystyrene or polystyrene-polyisoprene-polystyrene block copolymers are preferably chosen as

20   matrix material.

The plastic-matrix-material content of the monolayer is chosen sufficiently low, in any case lower than 30 wt.% relative to the total weight of the monolayer. Preferably, the content is lower than 20

25   wt.%, most preferably lower than 10 wt.%.

The fibre direction in each monolayer in the ballistic-resistant moulded article of the invention is rotated with respect to the fibre direction in an adjacent monolayer. This construction is hereafter

30   referred to as being "cross-layered". Good results are achieved when this rotation amounts to at least 45 degrees. Preferably, this rotation amounts to approximately 90 degrees.

The relatively high density and an SEA value

35   of at least 75 Jm^2/kg of the compressed stack of the invention can be achieved by taking a number of measures. It is possible for instance to ensure in a

number of stages in the manufacture of the moulded articles that as few low-density components, like air or from the polymer evaporated gasses as possible remain in the moulded article. This can for instance be accomplished by using a plastic of very low viscosity in impregnating the reinforcing fibres in the manufacture of the monolayer. It is also advantageous to spread the reinforcing fibres well during the impregnation process or to subject them to for instance ultrasonic vibration. As mentioned above, if multifilament yarns are used, it is important for a good spread that the yarns have a low twist. Furthermore, the plastic may be applied in vacuo. Each of these measures has a beneficial effect on the level of protection of a ballistic-resistant moulded article obtained with the monolayers but the level of protection of the moulded article of the invention is not attained or is attained only with great effort.

The invention also relates to a process for the manufacture of a ballistic-resistant moulded article in which monolayers are stacked cross-wise, whereupon the stack is compressed at a given pressure at an elevated temperature.

A process of this kind is disclosed in for instance WO 89/06190. It teaches that when the plastic matrix material is heated to its melting point, relatively low pressures are sufficient for shaping the moulded article. The pressures stated vary from 0.05 MPa to a maximum of 3 MPa.

It has now surprisingly been found that significantly higher SEA values than hitherto known in the state of the art can be attained by compressing and cooling the stack at a pressure of at least 5 MPa.

The pressure preferably is at least 7 MPa. In this way, the theoretical maximum density of the compressed stack is approached more closely and the level of protection against the impact of projectiles

is increased further. The pressure preferably is at
least 10 MPa, more preferably at least 13 MPa and most
preferably at least 15 MPa. Preferably, the pressures
during compression at an elevated temperature and
5   during cooling are the same.

Compression at an elevated temperature is
intended to mean that the moulded article is subjected
to the given pressure for a particular compression time
at a compression temperature above the softening or
10   melting point of the plastic matrix material and below
the softening or melting point of the fibres. The
required compression time and compression temperature
depend on the kind of fibre and matrix material and on
the thickness of the moulded article and can be readily
15   determined by one skilled in the art.

It has been found that in order for a high
SEA value to be attained it is necessary that after
compression at an elevated temperature cooling, too,
take place under pressure.
20   Cooling under pressure is intended to mean that the
given minimum pressure is maintained during cooling at
least until so low a temperature is reached that the
structure of the moulded article can no longer relax
under atmospheric pressure so that the SEA value cannot
25   decrease. This temperature is easy to establish by one
skilled in the art. It is preferred for cooling at the
given minimum pressure to be down to a temperature at
which the plastic matrix material has largely or
completely hardened or crystallized and below the
30   relaxation temperature of the reinforcing fibres. The
pressure during the cooling does not need to be equal
to the pressure at the high temperature, but it is
preferred that these pressures are equal. The pressure
loss resulting from shrinkage of the moulded article
35   and the press due to cooling must regularly be
compensated for so as to keep the pressure during
cooling constant or at least on a sufficient high

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level.

As the stack of monolayers is heated to the desired compression temperature, the pressure preferably is increased to the desired level in, preferably at least three, disconti- nuous steps. In this way, blisters are prevented from forming.

For the manufacture of a ballistic-resistant moulded article in which the reinforcing fibres in the monolayer are high-drawn fibres of high-molecular-weight linear polyethyle- ne, the compression temperature is preferably 115 to 130°C and cooling to below 70°C is effected at a constant pressure. Compression temperature here means the temperature at half the thickness of the moulded article.

In the process of the invention the stack may be made starting from loose monolayers. Loose monolayers are difficult to handle, however, in that they easily tear in the fibre direction. It is therefore preferred to make the stack from consolidated monolayer packages containing from 2 to 8, as a rule 2, 4 or 8, monolayers that are placed cross-wise. Consolidated is intended to mean that the monolayers are firmly attached to one another. Very good results are achieved if the monolayer packages, too, are compressed at an elevated temperature and cooled at a high pressure, preferably of at least 5 MPa.

US-3743561 describes a process for the manufacturing of composite structures or articles from reinforcing fibers in a two step process. In the first step an intermediate structu- re is manufactured. In a second step a number of intermediate articles are assembled to form the composite article. Although US-3743561 describes the objective of improving mechanical properties, no disclosure is given about ballistic properties of the structures or articles.

In another embodiment of the process of the inven- tion the ballistic-resistant moulded article is manufactured by a process whereby, in a first step, a semi-manufactured

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article is produced by forming a stack of cross-layered mono-
layers, which stack has an areal density of from 0.25 to 5
kg/m² and subsequently compressing this stack at an elevated
temperature and cooling this stack at a given first pressure
whereupon, in a second step, the semi-manufactured articles
are compressed onto each other at an elevated temperature and
cooled at a given second pressure, with the first

pressure being at least 5 MPa.

An advantage of this process is that, if the semi-manufactured articles are also compressed and cooled at a pressure of at least 5 MPa in the second
5   step, the moulded articles obtained have a higher SEA value than moulded articles manufactured in a single compression step at the same pressure.

Another important advantage of the above-mentioned process is that high SEA values are
10   attainable when the second pressure is relatively low, preferably at most 5 MPa. It has been found that good SEA values can be attained if the second pressure is lower than 5 MPa or even 3 MPa. A major advantage of this is that manufacturers of ballistic-resistant
15   moulded articles, who often do not have high pressure moulds (i.e. higher than 5 MPa) at their disposal, can still achieve the good properties of the ballistic-resistant moulded article of the invention using conventional moulding equipment.
20   The semi-manufactured articles can then be centrally produced in locations where a high-pressure mould is available, for example at the manufacturer of the monolayers or monolayer packages.

The invention also relates to the semi-
25   manufactured article for the manufacture of a ballistic-resistant moulded article of the invention that is obtainable by the first step in the above-mentioned process.

The semi-manufactured article has an areal
30   density of from 0.25 to 5 kg/m^2. An areal density lower than 0.25 kg/m^2 has the disadvantage that the SEA value of the ballistic-resistant moulded article ultimately obtained is lower. An areal density higher than 5 kg/m^2 has the disadvantage that there is little flexibility
35   in the choice of the areal density of the ballistic-resistant moulded article ultimately to be formed and that the cycle time for compressing the semi-

manufactured article becomes unacceptably long. Preferably, the areal density of the semi-manufactured article is between 0.5 and 2.5 kg/m².

It has surprisingly been found that, using the process of the invention, higher SEA values are attainable if the reinforcing fibres in the monolayers have a cross-section aspect ratio of at most 3. Cross-section aspect ratio is intended to mean the ratio of the longest to the shortest principal axis of a perpendicular cross-section of the fibre. Preferably, the aspect ratio is lower than 2, more preferably lower than 1.5. It has been found that high SEA values are obtained at low compressive pressures in ballistic-resistant moulded articles in which the filaments have a lower aspect ratio (being rounder). For the same reason, the filaments preferably also have a fineness of 1.5 denier per filament or more.

Furthermore, it has been found that, using the process of the invention, higher SEA values are attainable at comparable compressive pressures if the monolayers employed in the ballistic-resistant moulded article are obtained by impregnating reinforcing fibres with an aqueous dispersion which contains the plastic matrix material.

Furthermore, it has been found that, using the process of the invention, higher SEA values are attainable at comparable compressive pressures if the monolayers employed in the ballistic-resistant moulded article have a fibre weight higher than 25, more preferably higher than 50 g/m². Preferably, the fibre weight is at most 150 g/m², more preferably lower than 100 g/m².

The invention is illustrated by means of the following examples without being limited thereto.

Examples I and II and comparative experiments A and B

Material used:

A monolayer package consisting of four monolayers disposed cross-wise at an angle of 90 degrees. The fibres are high-drawn fibres of high

5　molecular weight linear polyethylene of make Dyneema SK66 (TM) with a strength of 32.5 cN/dtex, a modulus of 1015 cN/dtex and a fineness of 1 denier per filament with a cross-section aspect ratio of about 5. The monolayer contains 20 wt.% matrix material consisting

10　of Kraton (TM) applied from an aqueous dispersion. Kraton is a styrene-isoprene-styrene triblock copolymer. The areal density of the monolayer package is 135 g/m^2.

15　Procedure:

A number of the above-mentioned monolayer packages were stacked to yield a package whereupon the package in its entirety was placed between two platens of a standard press. The temperature of the platens was

20　about 125-130°C. The package was retained in the press until the temperature at the centre of the package was 115-125°C. Subsequently, the pressure was increased to a compressive pressure as stated in Table 1 below and the package was kept under this pressure for 15 min.

25　Next, the package was cooled to a temperature of 60°C at the same compressive pressure.

Test procedure:

The panels obtained were fired at in

30　accordance with the procedure set out in STANAG 2920. Use was made of a 7.62 x 39 mm Mild Steel Core (PS Ball M 1943) bullet weighing 8 grammes. The bullet used had been obtained from Messrs Sellier & Bellot, Czech Republic. The experimental density of the panels was

35　determined by accurate weighing and measurement of the volume using a Vernier calliper. The standard deviation according to this density measurement is 0.002-0.004

g/cm^3.

Results:

The v_{50} and SEA values as a function of the compressive
pressure are given in Table 1. The stated SEA value was
calculated from the total areal density of the
ballistic-resistant moulded article. Relative density
is intended to mean the ratio of the experimental
density of the panel ρ_P and the theoretical density of
the panel, which is defined by ($\rho_f\, m_f + \rho_k m_k$). The
theoretical density of the ballistic-resistant moulded
article as calculated from $\rho_f = 0.97$, $m_f = 0.8$ and $\rho_k = 0.943$ amounts to 0.965.

Table 1

	AD (kg/m^2)	compressive pressure (MPa)	V$_{50}$ (m/sec)	SEA (Jm^2/kg)	Relative density
A	33.5	1.0	591	42	0.969
B	33.5	2.5	668	53	0.974
I	33.8	7.0	825	81	0.990
II	26.9	16.5	772	89	0.992

The results indicate that, at equal areal density, the
ballistic-resistant panel of the invention has a
surprisingly higher SEA value than a panel with a lower
rel. density. The table also shows that the panel of
the invention can be obtained by choosing a compressive
pressure of at least 5 MPa.

Examples III-VI

Material used:

A monolayer package consisting of four monolayers disposed cross-wise at an angle of 90 degrees. The monolayer package differs from the monolayer packages referred to in Examples I and II only in respect of the fibres used. The fibres are high-drawn fibres of high molecular weight linear polyethylene with a yarn titre of 880 denier, a tensile strength of 37.3 cN/dtex, a tensile modulus of 1220 cN/dtex, an elongation to break of 3.7%, a fineness of 2 denier per filament and a round cross-section aspect ratio of about 1. The monolayer contains 20 wt.% matrix material consisting of Kraton (TM). The areal density of the monolayer package is 135 g/m^2.

Procedure and testing

Starting from the above-mentioned monolayer packages, ballistic-resistant moulded articles were produced at various compressive pressures and tested in the manner set out in Example 1. The ballistic-resistant panel obtained had an areal density equal to 25.9 kg/m^2 for all compressive pressures.

The results are given in Table 2.

Table 2

Example	compressive pressure (MPa)	V_{50} (m/sec)	SEA Jm^2/kg	relative density (-)
III	1.0	741	85	0.981
IV	2.5	768	91	0.988
V	7.0	913	129	0.996

Example	compressive pressure (MPa)	V_{50} (m/sec)	SEA Jm^2/kg)	relative density (-)
VI	16.5	939	136	0.995

Comparative Experiment C and Examples VII and VIII

In Comparative Experiment C and Examples VII and VIII, ballistic-resistant moulded articles were produced from monolayer packages as described in Example I in the manner described above. The compressive pressures in Comparative Experiment C and Example VII were 1 MPa and 7 MPa, respectively. In Example VIII, semi-manufactured articles consisting of 5 monolayer packages were first moulded at a first compressive pressure of 5 MPa, which semi-manufactured articles were then stacked and compressed at a second pressure of 1 MPa. In each case, the compressive pressure was kept at the same level during cooling. The results are given in Table 3.

Table 3

	AD (kg/m^2)	compressive pressure (MPA)	V_{50} (m/sec)	SEA (Jm^2/kg)
C	29.6	1	614	51
VII	33.8	7	825	81
VIII	29.1	5/1	739	75

Comparative Experiments D and E and Examples IX and X

As the first starting material (S1) a monolayer package available under the name of SpectraShield (TM) and consisting of four monolayers

disposed crosswise at an angle of 90 degrees. The
fibres are high-drawn fibres of high-molecular-weight
linear polyethylene of make Spectra 1000 (TM) with a
fineness of 5.5 denier per filament and a cross-section
5 aspect ratio of about 1. The monolayer was obtained by
impregnating the unidirectional fibres with a solution
of the matrix material Kraton (TM).

As the second starting material (S2) a
10 monolayer package was prepared by first preparing a
monolayer starting from Spectra 1000 fibres which were
impregnated with an aqueous dispersion (instead of a
solution as in S1) of the matrix material Kraton. The
yarn weight in the monolayer is 52 g/m^2, the matrix
15 content is 20%. Of these monolayers four-layer
monolayer packages were made.

The monolayer packages S1 and S2 were stacked
and compressed into ballistic-resistant moulded
20 articles as described above. In Comparative Experiment
D and Example IX starting material S1 was used, in
Comparative Experiment E and Example X starting
material S2 was used. The compressive pressures used
and the results are given in Table 4.
25

Table 4

Example		AD (kg/m^2)	compressive pressure (MPA)	V_{50} (m/sec)	SEA (Jm^2/kg)
D	(S1)	24.9	1	524	44
E	(S2)	22	1	598	65
IX	(S1)	24.9	5	761	93
X	(S2)	22	5	792	114

30

A comparison between Comparative Experiments D and E and Examples IX and X shows the great improvement in ballistic resistance. A comparison of the starting materials S1 and S2 in Examples VII and VIII shows the great improvement in ballistic resistance obtained when the monolayers have been prepared with an aqueous dispersion of the matrix material in combination with high-pressure compression.